JAN 29 1923

58—4

Proceedings of the American Academy of Arts and Sciences.

VOL. 58. NO. 4.— JANUARY, 1923.

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BY P. W. BRIDGMAN.

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3. VAINIO, EDWARD A.— Lichenes in Insula Trinidad a Professore R. Thaxter Collecti. pp. 129–147. January, 1923. $1.60.
4. BRIDGMAN, P. W.— The Effect of Pressure on the Electrical Resistance of Cobalt, Aluminum, Nickel, Uranium, and Caesium. pp. 149–161. January, 1923. $.75.

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Presented October 11, 1922. Received October 18, 1922.

Introduction.

In former numbers of the Proceedings of the American Academy [1] I have given data for the effect of pressure on the resistance of 39 of the elements. It is my intention to keep this work as up-to-date as possible by the revision of the previous data or the inclusion of new substances; this paper is in the nature of such a supplement to the former work. The first three of the metals above have been previously investigated, but I have now been able to obtain them in a state of considerably higher purity than formerly, so that a redetermination of the pressure effect was worth while. The pressure coefficients now found for these purer samples are of the order of 10% higher than the previous values. Measurements on uranium have not been made before; the specimen I had was presumably not of very great purity, but since even the sign of the coefficient was not known, and since as a general rule impurity does not greatly affect the pressure coefficient, it was of interest to make and record the measurements. The work on ceasium is not yet complete, but enough has been done to establish the existence of surprising phenomena for this element, and since it may be some time before I shall be able to complete the work, it seemed that announcement of the chief fact should not be delayed. I have found that caesium has a new polymorphic modification under high pressure, of smaller volume than the ordinary modification, but that the resistance of this new modification increases instead of decreases under pressure. Since caesium is the most compressible of the metals, this result may be of significance in suggesting what may happen to all metals at pressures sufficiently extreme.

Detailed Data.

Cobalt. The former sample of cobalt was obtained from Dr. Herbert T. Kalmus who had prepared it in the course of an investigation of the properties of metallic cobalt for the Canadian Government. This was one of the impurer of the samples which he prepared, but

since it was the only one he had left, I was glad to have the chance to make the measurements. I have now obtained indirectly, through the kindness of Professor C. C. Bidwell of Cornell University, one of the purest of Kalmus's specimens. Since the preparation of cobalt in the form of wire is a matter of some difficulty, involving the swaging instead of drawing of the metal in the early stages, and since there seems to be no commercial use for pure cobalt, it is not likely that material other than that of Kalmus will be available for some time.

The analysis of this sample was: Co 99.73, Fe 0.14, Ni 0.00, S 0.019, Si 0.02, and C 0.09.

The total impurity is seen to be 0.27%, against 1.30% of the former sample.

The diameter of this piece was 0.10 cm. and the length about 6 cm. Its compressibility had been previously measured; for this purpose it had been annealed and straightened by rolling between red hot iron plates. For these measurements of resistance, current and potential terminals were soft soldered near the ends, and measurements made with the potentiometer. The technique was exactly like that used with those metals formerly measured with the potentiometer, and has been fully described in the previous paper. Because of the low resistance of this sample and the smallness of the pressure coefficient, the individual readings did not have as great regularity as those on the previous sample, and I did not think it worth while to try for the temperature coefficient of the pressure coefficient by making readings at different temperatures.

Measurements were made at 30° over the pressure range of 12000 kg/cm². The accuracy was not high enough to detect departure from linearity with pressure. Discarding one point, the average deviation of the observed points from a straight line was 2.0% of the maximum pressure effect. The average pressure coefficient over the range of 12000 kg. was -0.0_6934, against -0.0_6865 of the former sample. The purer sample has the numerically larger coefficient. This seems to be true in the majority of cases, although there is no general rule here as in the case of the temperature coefficient.

The resistance was measured at 30° and 75° at atmospheric pressure. Assuming the relation between temperature and resistance to be linear, as it was for the former sample, the temperature coefficient between 0° and 100° is 0.00439, against 0.00365 for the other sample. The highest value which I find listed for cobalt is 0.0033.[2] The higher coefficient of the new sample is what would be expected because of its greater purity.

Aluminum. This was a specimen of quite unusual purity, of the following analysis: Si 0.014, Fe 0.007, Cu 0.003, Al (by diff.) 99.976. I extruded it from a diameter of 1.27 cm. to 0.081 cm., from this diameter drew it through steel dies to a diameter of 0.051 cm., annealed it at a temperature of 350°, wound it non-inductively on one of the bone cores used in previous work, made connections to the current and potential leads with spring clips at the two ends, and made the measurements in the regular way on the potentiometer. The length was such as to give an initial resistance of about 0.2 ohms.

The regular procedure in making the measurements was followed. Several preliminary seasoning applications of pressure were made, and runs were made at 0°, 30°, 50°, and 95°. The run at 75° failed because of a minor accident. At 0° the average arithmetical deviation of the observed points from a line (no discards) was 0.23% of the maximum pressure effect, at 30° (one discard) 0.13%, at 50° (two discards) 0.6%, and at 95° (one discard) 0.17%. The deviation from linearity was symmetrical about the mean pressure within the limits of error, so that the changes of resistance can be represented by a second degree expression in the pressure. In addition to these pressure measurements, the temperature coefficient at atmospheric pressure was determined by measurements at 0°, 30°, 50°, 75°, and 95° in this order, and then the measurements at 50° and 0° were repeated. The repeated readings agreed with the original ones within the limits of setting the slider of the bridge wire, showing no temperature hysteresis.

TABLE I.

ALUMINUM.

Temp. °C.	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000 kg.	Average 0–12000 kg.		
0	1.0000	$-.0_{4}4489$	$-.0_{3}3954$	$-.0_{4}4128$	−.00111	6000
25	1.1167	4418	4043	4135	95	6000
50	1.2334	4364	4087	4129	86	6000
75	1.3501	4336	4029	4088	103	6000
100	1.4668	4278	3879	3990	126	6000

The results are collected in Table I and Figure 1. The method of presenting these results is the same as that of the previous papers. The average pressure coefficient between 0 and 12000 kg. is that number which multiplied by 12000 gives the change of resistance produced by 12000 kg. pressure as a fractional part of the resistance at atmospheric pressure and the temperature in question. The instantaneous coefficients at 0 and 12000 kg. are $\frac{1}{R}\left(\frac{\partial R}{\partial p}\right)_T$, where R is the resistance at the pressure and temperature in question. The maximum deviation from linearity is in fractional parts of the resistance at 0° and atmospheric pressure. As an example, suppose that it is required to find the resistance of aluminum at 50° at 6000 kg. in terms of its resistance at 0° and atmospheric pressure as unity. The average coefficient at 50° to 12000 is $-0.0_5 4129$, and the initial resistance at

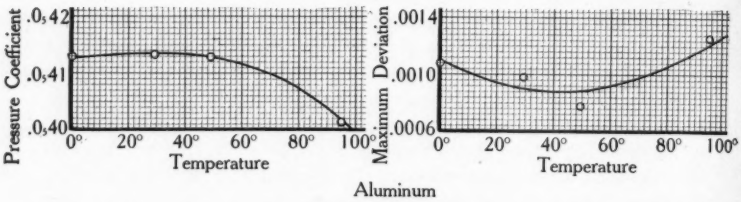


FIGURE 1. Aluminum, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0° C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

50° is 1.2334. If the change of resistance with pressure were linear, the decrease of resistance under 6000 kg. would be $1.2334 \times 6000 \times 0.0_5 4129$ or 0.03056. But the change of resistance is not linear, but as the sixth column shows, there is a deviation from linearity at 6000 of 0.00086, giving for the total decrease of resistance under 6000 0.03142, and for the actual resistance at 50° under 6000, 1.2020.

Compared with the results for the previous sample, the pressure coefficient of this is in general higher by eight or nine per cent. As a function of temperature, the pressure coefficient of this new sample shows a very flat maximum near the lower end of the temperature range, and from here on decreases. The pressure coefficient of the other sample decreased linearly over the entire temperature range. A decrease of the coefficient with increasing temperature is not what one might at first expect, but its reality seems vouched for by independent

measurement on two different samples. The maximum deviation from linearity of this new pure sample is not as simple as that of the less pure one; the former decreased linearly with rising temperature, whereas this new sample shows a minimum.

The temperature behavior at atmospheric pressure is worth comment. In the first place, the strict linearity with temperature is not usual. In the second place, the high value of the temperature coefficient of this piece as compared with the former sample, or the values of other observers, is to be noticed. The establishment of this high value removes aluminum from an apparently unique position with regard to its temperature coefficient. It is well known that practically all metals have a higher temperature coefficient in a condition of higher purity. Aluminum appeared to be the only exception, since the published values for samples of increasing purity have apparently become smaller with increasing purity.[3] But the purest of these previous samples had about 0.1% impurity. It is now seen that the apparent anomaly disappears in the region beyond 0.1%, the initial trend being reversed, and at sufficiently high purities the temperature coefficient increases with increasing purity, as it does for all other metals, and furthermore, the coefficient of the purest metal is higher than that of any of the impurer specimens.

Nickel. This was of exceptionally high purity, and I owe it to the kindness of Mr. I. B. Smith, of the Research Laboratory of Leeds and Northrup Co. I have already published data for the effect of tension on resistance,[4] and pressure on thermal conductivity [5] of this same nickel. Data for the compressibility are to be published shortly in These Proceedings. Hitherto it has not been possible to obtain in this country nickel of purity higher than that corresponding to a temperature coefficient of resistance of 0.0049. The coefficient of this was 0.00634, and is higher than any other published value except 0.00683 by Niccolai.[6] Except for the value of the temperature coefficient, I have no chemical analysis to indicate the purity.

The material was drawn by Leeds and Northrup to wire 0.0127 cm. in diameter, was annealed to redness, and then was double covered with silk insulation by the New England Electrical Works. It was wound non-inductively on a small glass core, seasoned at 135° for six hours, and subjected to three preliminary applications of 12000 kg. The initial resistance at 0° was about 115 ohms. The measurements were made on the Carey Foster bridge regularly used in measuring the changes of resistance of samples with high resistance.

The regular series of pressure measurements was made, at 0°, 25°,

50°, 75°, and 99°, and at the same temperature intervals there were also made two sets of readings of resistance as a function of temperature at atmospheric pressure, which agreed within the sensitiveness of setting the slider of the bridge. The accuracy of the pressure readings was as follows: at 0° the average arithmetical departure from a smooth curve (no discards) was 0.41% of the maximum pressure effect, at 25° (no discards) 0.32%, at 50° (one discard) 0.16%, at 75° (no discards) 0.34%, and at 99° (no discards) 0.24%. The average departure from linearity at the maximum was 0.9% of the maximum pressure effect.

TABLE II.

NICKEL.

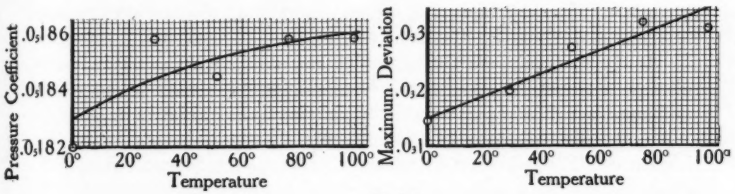
Temp. °C	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000 kg.	Average 0–12000 kg.		
0	1.0000	$-.0_51880$	$-.0_51819$	$-.0_51830$	−.000149	6000
25	1.1443	1899	1824	1843	198	6000
50	1.2975	1915	1827	1851	248	6000
75	1.4607	1925	1830	1858	297	6000
100	1.6345	1934	1832	1859	347	6000

The numerical results of the measurements are reproduced in Table II and Figure 2. The method of computation and presentation is the same as that used in the preceding papers.

Compared with the previous results on less pure nickel, the pressure coefficient of this is on the average about 15% higher, again verifying the observation that in most cases impurity depresses the pressure coefficient, but by a less amount than the temperature coefficient. The temperature coefficient of this piece is 0.00634, against 0.00487 of the previous sample, or an increase of 30%. The pressure coefficient of this new sample increases with rising temperature, as did that of the other sample, but the increase is much less rapid, and is not linear, becoming less rapid at the higher temperatures. The deviation from linearity of this new sample increases linearly with rising temperature, whereas that of the less pure sample at first passed

through a flat minimum, and then increased at the higher temperatures. The departure from linearity of this new specimen is furthermore symmetrical about the mean pressure, so that it can be represented by a parabolic formula, whereas that of the former sample was unsymmetrical, and there was a progressive shift of the pressure of maximum deviation with rising temperature.

Uranium. I am indebted to the kindness of Dr. A. W. Hull of the General Electric Company for a sample of this metal. This had been prepared with considerable difficulty for an investigation of its properties with a view to a possible commercial use. It turned out that its properties were not promising, so that no more will be prepared. This sample is probably unique, and I was most fortunate to obtain it. It was furnished in the form of rolled sheet, about 0.05 cm. thick,



Nickel

FIGURE 2. Nickel. Results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0° C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

0.7 cm. wide, and 4.5 cm. long. In this form the compressibility was measured, and I am reporting the results in another place. There were flaws in the specimen, which did not affect the compressibility measurements, since it was exposed to pressure all over, but which would have interfered with measurements of its electrical resistance. A small homogeneous sliver was cut from the sheet about 0.79 cm. wide and 2.2 cm. long. Uranium is very difficult to work, and the sliver had to be cut with a steel disc charged with diamond powder; I am indebted to the skill of Mr. David Mann for preparing the specimen.

The specimen was mounted for measurement with the potentiometer. It is not possible to solder leads to it. Fine grooves were filed around each end of the specimen, and a special spring clamp arrangement made by which the current and potential leads were

pressed tightly into the grooves. The potential terminals were 1.43 cm. apart, and the current terminals 2.0 cm. The small resistance of the specimen and the nature of the connections prevented measurements of the highest accuracy. Furthermore, it is probable that this specimen was not of high purity, because its temperature coefficient of resistance between 0° and 100° was found to be only 0.00230. In view of the impurity and somewhat low accuracy I made no attempt to find the temperature coefficient of the pressure coefficient, but made the pressure run at a single temperature, 30°. The resistance was found to decrease under pressure, as is normal for most metals. The sign of the pressure coefficient was the most important fact to be established by the measurement. The position of uranium as the heaviest of the elements at the end of the periodic table would have given particular interest to a possible positive pressure coefficient of resistance. The average arithmetical deviation of the observed points from a smooth line (no discards) was 1.6% of the maximum pressure effect. It was not possible to detect any deviation from the linear relation between pressure and resistance, and the average pressure coefficient over the range 0 to 12000 kg. was found to be $-.0_5436$.

The specific resistance of uranium seems not to be recorded in the literature. The specific resistance of this sample at 0° was 76.0×10^{-6}, which is high for a metal, being of the order of magnitude of the resistance of liquid mercury or bismuth.

Caesium. As already mentioned in the introduction, the results on caesium are preliminary, but because of their interest it seems worth while to briefly describe them. The preparation of pure caesium and its manipulation requires some practise, and I have not yet achieved final success. My original purpose in measuring the resistance of caesium was to search for a more pronounced drop in the temperature coefficient of resistance at high pressures than was found in the case of potassium. It would be expected that there would be such a phenomenon here because of the chemical similarity of caesium and potassium, and because of the much greater compressibility of caesium. This search failed, however, because of the entrance of a new polymorphic form at high pressures.

The material for the measurements was obtained from the Foote Mineral Co. of Philadelphia. I am also indebted to the kindness of Professor Baxter and Professor G. N. Lewis for other samples, but I was not successful in the manipulation of these. The two samples from the Foote Mineral Co. were provided in glass tubes sealed under oil. One of the samples was apparently somewhat purer than the

other; its melting point appeared to be sharper and its yellow color not so pronounced. These samples were transferred to capillaries of thin glass provided with four platinum terminals sealed through the glass, two for current and two for potential leads. The measurements were made in the regular way on the potentiometer. The details of the method of transferring to the capillary need not be described; it is possible to improve it.

Measurements were made on the first and purer sample with a view to establishing the temperature coefficient over the range 0 to 12000 kg. In order to avoid melting at atmospheric pressure, the temperature range of the measurements was low, from 0° to 16°. Over this range of pressure and temperature the most puzzling results were found. At low pressures the resistance apparently decreased greatly with increasing pressure, which was the result expected, but at higher pressures the resistance increased again. After a day's run, the apparatus was taken apart in the search for trouble, and the glass capillary was found cracked, so that air got at the caesium and destroyed it. The crack in the capillary had no effect on the measurements, however. The temperature coefficient of this first and purer sample between 0° and 16° was found to be 0.0054, which is high, and evidence of good purity.

The second sample, as already stated, seemed to be less pure initially, and during the manipulation received further impurity because of the accidental access of a small quantity of air to the inside of the apparatus during the transfer to the capillary. This heightened the yellow color and dirtied the metal so that it left a yellow scum on the glass, whereas the first sample had run as cleanly through the glass as clean mercury. However, the impurities introduced in this way were obviously non-metallic, and there is no reason to expect that this impurity introduced any essential change in the phase relations of the different polymorphic forms.

With the information received from the first sample it was possible to direct the measurements on the second sample much more intelligently, and to definitely establish the more important features. In the first place it was established that caesium has a new modification at high pressures, that the transition point is sharp, as it should be for a true transition, and that the transition pressure varies with the temperature. Two measurements were made of the transition pressure at 0°. The first of these established that the equilibrium point was contained between two pressure limits 140 kg. apart, and that the mean point was 1960 kg. The second measurement shut the transi-

tion within limits 100 kg. apart, at a mean pressure of 1990 kg. We take as the most probable transition pressure at 0°, 1980 kg. At 17° the transition was shut between two limits 400 kg. apart, mean 3260 kg. The transition curve is therefore of the normal type, rising to higher temperatures at higher pressures, and the phase stable at the higher temperature has the greater volume. Unless the transition line has exceptionally great curvature, it should be possible to find the

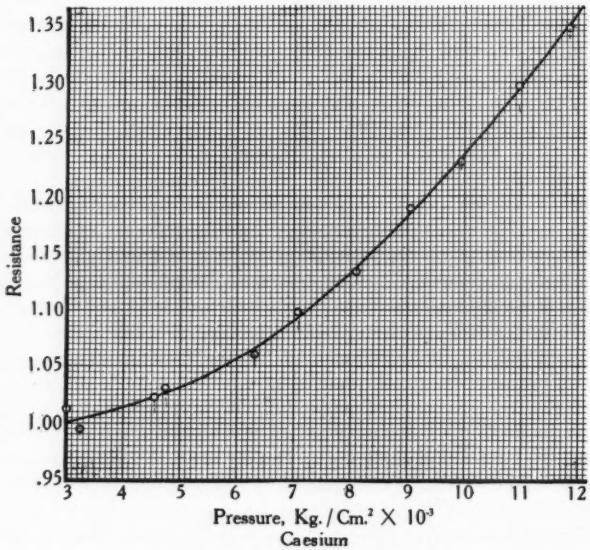


FIGURE 3. Caesium. The resistance at 0° C. of the new high pressure modification of caesium as a function of pressure in terms of its resistance at 0° C and 3000 kg/cm² as unity.

new modification at atmospheric pressure at some temperature below 0°; linear extrapolation gives −26° as the atmospheric transition temperature.

The electrical properties of the high pressure modification were found to be abnormal in that the resistance increases with increasing pressure. This makes the sixth metal now known with this property, the others being bismuth, antimony, calcium, lithium, and strontium.

It was possible to make fairly satisfactory measurements of the resistance of the new modification at 0° from the transition pressure out to 12000 kg. On the first application of pressure the results were irregular. This is due to the cracking of the glass capillary under pressure and the consequent change in the geometrical configuration of the caesium due to its extreme softness, but after the seasoning produced by the initial application of pressure the results were regular and would repeat. (The results obtained with the first sample were irregular for the same reason, but no results were found with the first sample that were inconsistent with those given by the second.) The experimental results are reproduced in Figure 3 plotting the measured resistances in terms of the resistance at 3000 kg. as unity. The curve shown was obtained with increasing and decreasing pressure; the points alternately are those with increasing or decreasing pressure. The curve is the same in character as that obtained for the five other abnormal metals in that the curvature is upward, or the resistance increases at a continually increasing rate at the higher pressures. This is most important as suggesting what the mechanism of conduction may be, and is just what would be expected on the basis of theoretical considerations which I have already described. The magnitude of the pressure coefficient is high; between 11000 and 12000 kg., the average pressure coefficient of resistance is 0.000493, which is about the same as that of strontium, which has the highest coefficient of the abnormal metals hitherto measured.

At the transition point there is a discontinuity in resistance in the normal direction, that is, the high pressure phase, or the phase with the smaller volume, has the smaller resistance. I know of no exception to this rule. At 0° the resistance of the high pressure modification at the equilibrium pressure is 0.407 that of the low pressure form.

I am indebted to my assistant Mr. I. M. Kerney, for help in making many of the readings.

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